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LIMITATIONS IN THE USE OF PARTITIONING TRACERS FOR ESTIMATING THE VOLUME AND DISTRIBUTIONS OF NAPLS

THESIS

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Abstract

Partitioning tracers offer a unique alternative to inefficient and expensive traditional methods of detecting NAPL contamination in the subsurface. In order for partitioning tracers to be effective, however, several assumptions must be true. One of the major assumptions is that once injected, the tracer will contact all of the NAPL present in the flow field. If this assumption is not reasonable, the result will be an underestimation of the true NAPL volume.

This thesis looked at the impacts of NAPL distribution and average NAPL saturation of a porous medium on the ability of partitioning tracers to contact all of the NAPL present. Models of a simple homogeneous aquifer were developed using the Groundwater Modeling System (GMS). Partitioning tracer tests were then simulated using the FEMWATER flow and transport code. Simulations were performed for different types of NAPL distribution (i.e., ganglia and pools) and different average NAPL saturation values. The simulation results were used to develop concentration breakthrough curves for the tracer at the point of extraction.

Because complete recovery of the tracer mass was not observed, extrapolation of the breakthrough curve was required to account for the remaining tracer. These mass balance problems prevented drawing direct conclusions regarding the impact of NAPL distribution and saturation on the effectiveness of the tracer method. However, the results did emphasize the impact of the uncertainty associated with interpreting breakthrough data generated from tracer tests. It also provided insight into specific model parameters that most likely contributed to mass recovery problems including specified boundary conditions and the injection/extraction well system schematic. If some of the problems evident in this

research are corrected, numerical models could prove to be a very effective and inexpensive tool for studying the partitioning tracer method.

Limitations in the Use of Partitioning Tracers for Estimating the Volume and Distribution of NAPLS

I. Introduction

Background

Over the past two decades, the Department of Defense (DOD) has spent millions of dollars investigating past environmental contamination problems at various military installations throughout the country. DOD must now implement appropriate remediation techniques to solve these problems in a period of budget reductions. One of the biggest problems on many installations is contaminated groundwater. This problem is especially important because groundwater contaminated on DOD property can migrate off site and pose adverse environmental and health risks to local communities.

In order to treat the source of contamination, one must have an adequate understanding of the amount and location of that source. Nonaqueous phase liquids (NAPLs) in the saturated zone are a common source of contamination that present a unique problem for site investigators. Due to their physical and chemical properties, and the complex soil pore geometries that exist in the subsurface, once introduced into the soil (from spills, leaking underground storage tanks (USTs), etc.), NAPLs distribute in a very unpredictable manner. This distribution makes it extremely difficult to quantify the volume of NAPL and determine its location within the aquifer. Once in the aquifer, NAPLs present a constant (until they completely dissolve) source of contamination as they partition into passing groundwater. Most NAPLs have high enough solubility to cause contamination in excess of drinking water standards (Poulsen and Kueper, 1992).

NAPLs are classified as dense (i.e., heavier than water) or light (i.e., lighter than water). Beneath the surface, they can exist as either a residual phase (small globs within pore spaces) or pools that collect on top of confining layers. The density of the contaminant, whether dense (DNAPL) or light (LNAPL), will dictate whether or not it will float or sink in water. Capillary forces within the porous medium are the primary forces that dictate if and how a NAPL will migrate and distribute through the vadose and saturated zones (Mercer and Cohen, 1990).

In the past, the most common methods used for detecting NAPLs consisted of conducting chemical analyses on core samples obtained from contaminated aquifers (for DNAPLs) or installing monitoring wells in locations where the NAPL was believed to exist (for LNAPLs) (Jackson et al., 1995). These techniques were often very time consuming and expensive ventures that yielded little chance of success. The use of "tracers" that partition into the NAPL phase has provided a seemingly viable alternative to these unsatisfactory conventional methods. As the tracers partition, they are "retarded" in proportion to the amount of NAPL present. This retardation results in a longer tracer travel time between injection and extraction. Therefore, comparing this time to that of a nonsorbing tracer can yield an estimation of NAPL volume (Annable et al., 1995).

The theory behind the partitioning tracer method is based on several key assumptions. One major assumption is that the tracer contacts all of the NAPL present in the flow field. This full contact could strongly depend on how the NAPL is distributed in the aquifer. Mass transfer limitations due to low interfacial area can reduce the retardation of the partitioning tracer leading to underestimation of the NAPL volume (Annable et al., 1995). Another factor that may affect the effectiveness of partitioning tracers is the ratio of existing NAPL volume to the pore volume of the contaminated aquifer (i.e. average NAPL saturation). A small average NAPL saturation value could result in tracer retardation too small to discern due to soil retardation, error, etc.. On the other hand, a high degree of saturation may create more mass transfer constraints and thus create problems recovering all of the tracer mass.

Importance of Research

The United States Congress has recently expressed concern regarding excessive study and lack of remedial action in the DOD environmental program. In doing so, it significantly reduced the budget allowed for site investigation and study. Environmental managers and regulators are constantly looking for more cost effective and faster methods for site characterization. The use of partitioning tracers for NAPL detection could provide DOD with a more efficient method for locating and quantifying sources of groundwater contamination. However, before DOD invests its limited resources in this method, it is imperative to research the validity of the assumptions on which the partitioning tracer theory is based. This research can help identify the limitations of partitioning tracers and determine their applicability in various remediation efforts.

Purpose Statement and Research Objectives/Questions

The purpose of this study is to investigate possible limitations of the partitioning tracer method for estimating NAPL volumes and thus determine its applicability and effectiveness in Air Force remediation efforts.

The two main questions that are investigated in this research are 1) What is the impact of particular NAPL distributions on the partitioning tracer technique? and 2) What is the impact of the average NAPL saturation on the partitioning tracer technique?.

Thesis Overview

This thesis consists of four major sections. These include the Literature Review, Methodology, Findings and Analysis, and Conclusions. The Literature Review section provides a summary of the major concepts associated with the research. The Methodology section describes the approach to the problem and a detailed description of the procedures used to complete the experiments necessary to achieve the research objectives, including an explanation of the Groundwater Modeling System (GMS) software and the FEMWATER flow and transport code used in the experiments. The Findings and Analysis section provides a summary of the experimental results and an assessment of what the results indicate. The Conclusions section provides a final summary of the research, assesses how the findings and analysis address the research questions, and discusses recommendations regarding possible future research to investigate the use of partitioning tracers for NAPL detection.

II. Literature Review

Introduction

The partitioning tracer method for detecting and quantifying NAPL contamination involves injecting and extracting various tracer chemicals that are allowed to travel through a contaminated flow field. This technique takes advantage of an organic tracer's property of partitioning between water and subsurface NAPL. A comparison of the travel times for a nonpartitioning tracer (i.e., one that does not retard) with one that does partition provides a method of estimating the volume of NAPL in the established flow field. The key variables required to obtain these estimates include the NAPL-water partition coefficient (K_{Nw}) and the average travel times of both the nonpartitioning and partitioning tracer (t_n and t_p respectively).

In order to understand how the numerical experiments in this research were developed, it is imperative to have an understanding of the concepts that influence the partitioning tracer method and how the variables required for estimating NAPL volumes are determined. This Literature Review section focuses on summarizing previous research to help gain an in-depth knowledge of the various concepts considered during the investigation of the partitioning tracer method for NAPL detection. These concepts include NAPL distributions, partitioning theory, first moment analysis, and partitioning tracer tests. This section also summarizes how previous research provides additional academic justification for further research in this area.

NAPL Distributions

The models developed for this study simulated NAPL contamination. The effectiveness of the partitioning tracer method could depend heavily on the manner in which the NAPL is distributed. This is because the distribution dictates how much of the NAPL will come in contact with the tracer. Therefore, the first step in determining how to simulate NAPL contamination is to understand how it is distributed in the subsurface.

NAPL distributions ultimately depend on how the fluid migrates through the subsurface. Several properties of both the NAPL and porous medium influence NAPL movement. Important NAPL properties include density, viscosity, and hydrophobicity. LNAPLs, as bulk fluids, migrate according to subsurface pressure and elevation head gradients and often end up in lower levels of the water table and capillary fringe (Mercer and Cohen, 1990). DNAPLs can travel below the water table (i.e., into the saturated zone) where transport is strongly influenced by capillary forces and low permeability layers. Viscosity dictates how fast the bulk fluid NAPL will travel as well as influences the transport by molecular diffusion. The hydrophobicity of the various NAPL components affects solubility, sorption onto aquifer solids, and interfacial tension (Heyse, 1994).

In addition to the NAPL properties that dictate movement, subsurface characteristics also have a significant impact on how NAPLs are distributed. The permeability of the soil impacts how easily fluids travel through it. Although NAPLs preferentially travel through the paths of least resistance to flow (i.e., most permeable), it is often difficult to determine the exact route because of the large number of different permeable layers that may exist in the subsurface.

In general, NAPLs distribute themselves as disconnected ganglia (residual) or as thin, potentially mobile pools (Poulsen and Kueper, 1992). The ultimate NAPL distribution depends heavily on the pore size distribution and the bedded structure of the porous media (Mercer and Cohen, 1990). The fraction of the pore space occupied by NAPL is referred to as the NAPL saturation (S_N) and is defined in Equation (1):

$$S_N = \frac{V_{NAPL}}{V_{voids}} \tag{1}$$

where V_{NAPL} is the volume of NAPL, and V_{voids} is the total volume of pore space in the porous medium (Conrad et al., 1992). The subscript N refers to the NAPL phase.

Several field and laboratory experiments have been conducted to gain a better understanding of how NAPLs are distributed. Conrad et al. (1992) and Powers et al. (1992) point out that most existing mathematical models assume residual contamination exists as perfectly spherical “ganglia”. Their laboratory experiments, however, indicate that the ganglia can exist in very irregular “branched” shapes. These continuous ganglia may occupy several pore spaces and the connecting channels between them. The geometry is significant because it suggests that most of the organic contaminant will not come in contact with a passing tracer. With only the heads of the branched ganglia exposed, a tracer may only contact a small portion of the NAPL present. The result would be an underestimation of the true NAPL volume.

In the saturated zone, NAPLs can distribute quite differently than in the vadose zone. Anderson et al. (1992) discovered that when dense chlorinated solvents (DNAPLs) infiltrate the saturated zone, the interface between the NAPL and the displaced water becomes unstable. The result is that NAPL distributes in unpredictable vertical “fingers” rather than the more uniform residual distribution often seen in the vadose zone. If the finger encounters a low permeability layer, lateral spreading (pools) will also occur. This type of distribution can have significant impacts on the effectiveness of current detection methods. For example, vertical migrating fingers can result in much greater penetration depth of the solvent compared to more uniform distributions. Also, the formation of fingers essentially creates several contaminant sources that exist in very unpredictable locations. These factors make it even more difficult for investigators to locate NAPL and reemphasize the need for more efficient methods that can cover larger volumes (e.g., the partitioning tracer method).

Although research has provided a better understanding of the characteristics of various types of residual distributions, less is known about NAPL pool distributions. The biggest reason for this is that the majority of pools form at the bottom of aquifers making them extremely difficult to locate and study. The fate of DNAPLs depends on the relief patterns of the deepest portions of the subsurface "whose course in comparison with the groundwater table is usually unknown" (Schwille, 1981).

Despite the lack of success with in situ studies, researchers have attempted to model pools to determine both their contribution to groundwater contamination and their source "life" compared to residual distributions. Although more difficult to predict, the contact area of residual NAPL with the passing groundwater is much greater than that of an equivalent mass of a NAPL pool. Therefore residual NAPL will dissolve quicker and exist for shorter periods of time (Mercer and Cohen, 1990). This is because the ganglia exists throughout the depth of the aquifer where water can contact it on all sides whereas only the tops of pools are exposed to passing groundwater.

To investigate the impact of distribution on mass-transfer, Anderson et al. (1992) conducted a modeling experiment that compared finger distributions with NAPL pools. The results indicated that the fingers did indeed dissolve much faster than pools, implying the major long term sources of contamination exist as pools. Lee et al. (1992) also state that “patterns of residual fuel entrapment” can significantly contribute to mass-transfer constraints between the NAPL and groundwater. Because it can be assumed that tracers contact the NAPL to the same extent as the groundwater, experiments such as these suggest that the type of distribution present could significantly impact tracer performance. More specifically, they suggest that distributions consisting of NAPL ganglia will more likely be detected by partitioning tracer than NAPL pool distributions.

The type of distribution can also impact relative permeability. As the saturation of NAPL increases, the ability of the water carrying the tracer to flow through pore spaces containing NAPL decreases. Again, this may adversely affect the tracer’s ability to contact the NAPL. The NAPL saturation of pools is usually much larger than that of ganglia distributions. In other words, NAPL volume in a pool distribution takes up less pore volume than an equivalent NAPL volume existing as ganglia. Because of this, it is more difficult for a tracer to effectively reach pooled NAPL. This again suggests that the partitioning tracer method is most effective when applied to ganglia distributions.

Another factor that requires consideration is the average NAPL saturation of the aquifer itself, that is, the actual NAPL volume per volume of aquifer. Whether the tracer method is more effective on larger or smaller volumes of contamination is an issue of importance to site investigators. This research will address this issue by comparing results from scenarios with different average NAPL saturation values.

Past research provides a strong indication of how complicated and unpredictable NAPL distributions in the subsurface can be. This is important to this study in three ways: (1) it emphasizes the need for better methods, such as the use of partitioning tracers, for locating and quantifying NAPL contamination before remedial actions can be implemented; (2) it helps illustrate the potential impact the NAPL distribution has on the effectiveness of the tracer method; and (3) it helps determine how to best simulate NAPL contamination for this study.

Partitioning Theory

Because the effectiveness of the tracer method depends on the ability of a particular tracer to partition into the NAPL phase, a sound understanding of partitioning behavior is imperative. There has been much research to better understand how various organic pollutants partition into the aqueous phase. Most of the theory developed in this research can also be applied to how organic tracers partition between water and NAPLs. Attention must also be given to how organic tracers are sorbed by organic material of the aquifer solids.

The term "partitioning" (also called dissolution or absorption) refers to the process by which a chemical distributes between different phases in the subsurface. The partitioning processes of interest in this research include the distribution of the tracer between the aqueous and NAPL phases and between the aqueous and solid phases (sorption). Equilibrium partitioning between the NAPL and aqueous phases is described by Equation (2):

$$K_{Nw} = \frac{C_N}{C_w} \tag{2}$$

where C_N is the concentration of contaminant (or tracer) in the NAPL phase and C_w is the concentration in the water phase at equilibrium (Annable et al., 1995). The NAPL-water partitioning coefficient, K_{Nw}, indicates how well the tracer will partition into the NAPL phase. Estimated values of K_{Nw} for various tracers are usually determined in laboratory batch and/or column tests or estimated from a number of predictive equations that have been developed. Most of these equations are based on properties such as the chemical structures of the organic compounds and similarities to compounds with known K_{Nw} values (Scwarzenbach et al, 1993).

When assuming ideal partitioning behavior (i.e., Raoult's law applies), the value of KNw can be estimated by Equation (3):

$$K_{Nw} = \frac{1}{V_o \cdot S_1} \tag{3}$$

where V_o is the molar volume of the organic phase and S_l is the hypothetical super-cooled liquid solubility (Lee et al., 1992). Because the validity of this assumption impacts the accuracy of estimated values of K_{Nw}, it in turn impacts the accuracy of the tracer's estimation of the NAPL volume. Deviations from ideality have led to higher aqueous concentrations (C_w) compared to predictions based on Raoult's law (Cline et. al, 1991). Thus, if non-idealities do exist in the field, actual K_{Nw} values will be smaller than predicted values. An assumption of ideality could thus result in an underestimation of the true NAPL volume.

Several researchers have investigated the potential extent of deviations from ideal behavior for several different organic compounds (Burris and MacIntyre, 1986, Cline et al., 1991, Lee et. al, 1992, Chen et al., 1994). Laboratory batch measurements of K_{Nw} for several polycyclic aromatic hydrocarbons (PAHs) were compared to results obtained from the UNIQUAC functional group activity coefficient (UNIFAC) model that quantifies and accounts for potential non-idealities (Lee et al., 1992). The results indicated that the differences between the two estimates were small and thus the effect of non-ideality was negligible. At least some of the differences were attributed to uncertainty in the solubility estimates (S_1) and solute activity coefficients. The researchers concluded that Raoult's law could most likely be used to predict values of K_{Nw}, within a factor of two, for most field-scale problems.

Other experiments using a similar approach investigated the potential effects of "mixtures" of various volatile organic compounds (VOCs) in gasoline (Cline et al., 1991) and motor oil (Chen et al., 1994). Both experiments concluded that despite the complexities of the different compounds, the assumption of ideality is adequate for field-scale applications provided no mass-transfer limitations exist (i.e., equilibrium conditions prevail). This is important because this research involves simulations of field-scale applications.

As a contaminant (or tracer) moves with the groundwater through the subsurface, its transport is delayed by partitioning into various organic phases that may exist in the porous medium. This delay is referred to as retardation. The retardation of a tracer partitioning into NAPL is described in Equation (4):

$$R = 1 + K_{Nw} \cdot \frac{S_N}{(1 - S_N)} = \frac{t_p}{t_n} \tag{4}$$

where t_p and t_n are the average travel times for the partitioning tracer pulse and a non-partitioning tracer pulse, respectively (Annable et al., 1995). A nonpartitioning tracer has a K_{Nw} value at or near zero and will not experience any retardation as it travels through the flow field. Comparing the travel times between a tracer that partitions with one that does not allows one to quantify the retardation factor. The amount of retardation is related to the amount of NAPL present in the flow field (i.e., S_N). This concept is employed to quantify NAPLs with partitioning tracers.

The other partitioning relationship of interest exists between the tracer and the aquifer solids. A contaminant (or tracer) may be sorbed by organic carbon in the solids, also causing retardation. A sorption isotherm describes the partitioning of a tracer between the aqueous and sorbed phases. Because the concentration of tracers used in tests are relatively low, the linear isotherm is usually assumed. The linear isotherm can be described by equation (5):

$$S = K_p \cdot C \tag{5}$$

where S is the mass of solute sorbed onto the solids, K_p is the sorption partition coefficient and C is the concentration of solute in solution (Karickhoff, 1979).

For hydrophobic organic compounds, K_p can be estimated from the fraction of organic carbon content (f_{oc}) as shown in Equation (6):

$$K_p = K_{oc} \cdot f_{oc} \tag{6}$$

where K_{oc} is the partition coefficient of a compound between organic carbon and water (Karickhoff et al., 1981). K_{oc} can be estimated from the Karickhoff et al., (1981) regression equation:

$$\log K_{oc} = \log K_{ow} - 0.29 \qquad (7)$$

where K_{ow} is the octanol/water partition coefficient. Values of K_{ow} for many organic compounds have been determined experimentally and can easily be found in the literature. When compared to literature measurements, values of K_{oc} estimated from Equation (6), generally agreed within a factor of three. Most of the uncertainty associated with these values was attributed to the difficulty in experimentally measuring compound solubilities. The parameter, f_{oc}, is usually obtained from laboratory measurements of samples from the porous medium of interest.

Partitioning of the tracers in both the NAPL and sorbed phases must be considered when conducting tracer experiments. All of the retardation experienced by the tracer is assumed to be from partitioning into NAPL. However, if there is significant sorption to soil, some of the retardation should be attributed to this sorption. The retardation due to sorption of the tracer by organic solids is:

The total retardation due to partitioning into NAPL and soil is:

$$R = 1 + \frac{\rho_B \cdot K_d}{n \cdot (1 - S_N)} + \frac{S_N \cdot K_{NW}}{(1 - S_N)} \qquad (8)$$

where ρ_B is the bulk density and n is the porosity of the solids matrix.

The partitioning tracer method is used to estimate NAPL volumes by quantifying the extent of retardation a tracer undergoes while traveling through a flow field. However, the amount of retardation due to sorptive processes (i.e., not due to partitioning into NAPL) is usually unknown. This uncertainty can have a significant impact on the accuracy of the NAPL volume estimates obtained from this technique. If the extent of sorption is underestimated or assumed to be zero when in fact significant sorption is present, the result will be an overestimation of the true NAPL volume. This is because more of the retardation will be attributed to NAPL partitioning than actually occurs. Although the effect of sorption is an important issue that requires more investigation, it will not be considered in this research.

Method of Moments

Aris's method of moments is a common tool used in the analysis of contaminant transport (Goltz and Roberts, 1987). Applied to solute concentration breakthrough data, it provides a means of estimating spatial and temporal parameters of interest such as mass, travel time, and dispersion coefficients. A breakthrough curve is a graphical representation of concentration versus time at a particular point in the flow field. The breakthrough curve is defined by tracer concentrations in the extraction well for tracer experiments. The first temporal moment is calculated from the breakthrough curve, which is used to compute the average travel time of the tracer through the flow field.

The first temporal moment is defined by equation (9):

$$m_{1,t} = \int_0^\infty t \cdot C(x,t)dt \qquad (9)$$

where the tracer is first introduced into the injection well at t = 0, and C(x,t) represents the solute breakthrough curve at a distance, x, from the injection well (Goltz and Roberts, 1987). The normalized form of the first moment represents the average arrival time of the solute mass at the extraction well (Equation (10)):

$$\mu_{1,t} = \frac{m_{1,t}}{\int_0^\infty C(x,t)dt} \tag{10}$$

where the denominator represents the zeroth absolute moment (total mass of solute) (Goltz and Roberts, 1987).

For a tracer pulse source of finite duration t_d, the average travel time is the average time of arrival minus the average time of injection as shown in Equation (11) (Jin et al., 1994):

$$\mu_{1,t}* = \mu_{1,t} - \frac{t_d}{2} \tag{11}$$

Equation (11) is used to obtain values of average travel time for a pulse of both a partitioning and non-partitioning tracer (t_p and t_n, respectively).

Once the values of t_n and t_p are obtained, they can be used in Equation (3) to determine the retardation factor. This equation can then be rearranged to obtain an estimate of the average saturation (S_N):

$$S_N = \frac{R-1}{K_{NW} + (R-1)} \tag{12}$$

The estimated value of S_N can then be multiplied by the pore volume to obtain an estimate of NAPL volume:

$$V_{NAPL} = S_N \cdot V_{MEDIA} \cdot n \tag{13}$$

Goltz and Roberts (1987) point out that although spatial moments are dependent on the mass transfer rate, temporal moments are not. Therefore, local equilibrium is theoretically not necessary for this method to be valid.

Detection limits from current measurement methods may have an impact on the ability of site investigators to accurately apply the method of moments to breakthrough data generated from tracer experiments. Tracers experiencing retardation can exhibit "tailing" in the breakthrough curve, as demonstrated by very low concentrations arriving at long times. The tailing effect is due to interphase (i.e. NAPL, and sorbed phases) mass transfer limitations experienced by the tracer. At some point, the concentrations will be too small to measure although tracer mass will still be present in the extracted groundwater. The impact of this phenomenon is also the subject of this research.

Partitioning Tracer Tests

Both laboratory and field scale experiments have been accomplished to determine the feasibility of using partitioning tracers for NAPL volume estimation. Jin et al. (1994) performed both laboratory column experiments and computer simulation tests to investigate the partitioning tracer's ability to estimate NAPL contamination and assess remediation performance. The column test consisted of first establishing a residual saturation of tetrachloroethylene (PCE) followed by the injection of two alcohol tracers. The column was then flushed with several pore volumes of distilled water until no tracer was evident in the effluent. The experimenters applied the method of moments to the resulting breakthrough curves in order to compute the NAPL volume detected by the tracers. They also used a method of inverse modeling for a more detailed analysis of the actual spatial distribution of the contaminant.

The computer simulation consisted of a hypothetical aquifer characterized similar to the Borden site (Jin et al., 1994). A simulated point source of PCE was introduced and the contamination was allowed to distribute throughout the porous medium. The resulting distribution consisted of a well defined residual phase of PCE. A surfactant enhanced remediation was then conducted with tracer tests being simulated at various phases to determine the remediation effectiveness.

The results from both the experimental and simulation studies yielded positive evidence that the use of partitioning tracers can indeed be an effective tool for detecting and estimating NAPL contamination. They also highlight the potential use of tracer tests not only for site characterization, but also for assessment of remediation effectiveness.

Annable et al. (1995) conducted field experiments at Hill AFB, Utah using several different tracers to estimate NAPL volumes. The field techniques were combined with first moment analysis to calculate volumes based on tracer retardation. For this experiment, a test cell was constructed on a site already contaminated by LNAPL. The cell was flooded to create a well defined smear zone of contaminant. This was done to improve the chances of contact between the LNAPL and tracer. The experiment demonstrated that partitioning tracers can be used successfully for estimating NAPL contamination in the field.

It is important to note that in both experiments, the researchers were able to create environments that were nearly ideal for demonstrating the use of partitioning tracers.

Therefore the potential limitations already discussed (e.g. the potential impact of NAPL distribution) had little, if any, impact on the results. However, before limitations can be studied, experiments like these are necessary to determine if new technologies are even feasible. Therefore, the success of these experiments suggests the need for more study before real world applications.

Conclusion

Despite the encouraging results, the researchers in both the laboratory and field experiments were quick to point out the various criteria that must exist in order for successful results in the field. These include tracers that are environmentally acceptable, reasonably priced, and readily available. Perhaps more importantly, previous experiments indicate several site specific requirements or assumptions that must be met. These include:

1. Tracer retardation by sorption to aquifer solids does not contribute enough uncertainty to affect the NAPL volume estimate from the tracer method.
2. NAPL-water partition coefficient is constant in space and linear, and either known or reliably predicted.
3. Mass transfer constraints do not cause enough tailing so that first temporal moment is underestimated.
4. Tracer effectively contacts all NAPL existing in the flow field.

The validity of these assumptions is integral in assessing the accuracy of the partitioning tracer method. Assumption 4 is the main focus of this research. The experiments presented in this thesis include simulations of different NAPL distributions with various NAPL saturation values. This allows investigation of the potential impact of distribution type on the ability of the tracer to contact the NAPL. The simulations also include different average NAPL saturation values. This provides a means of observing how the percentage of volume occupied by NAPL impacts how well the tracer contacts the NAPL. Finally, the breakthrough curves obtained from the various simulations are used to determine if mass transfer constraints (tailing) impact the use of first moment analysis enough to significantly impact the estimates of NAPL volume.

Because the tracer method is a relatively new technology, it is understandable why research up to this point has been limited. However, in the experiments that have been performed, the need for further research is not only evident but specifically stated by the researchers. By stressing the potential limitations associated with and the specific criteria needed for successful tracer tests, the literature provides additional justification for the type of research presented here.

III. Methodology

Introduction

This section describes the approach taken to address the research questions listed in Chapter I. Included is a summary of the research design, a description of the GMS system used to develop the models used for the simulations, a description of how the scenarios (porous media and NAPL distributions) were developed for the simulations, and an explanation of how the various input parameters for the model were chosen.

Research Design

The design involved first creating a conceptual model of a simple aquifer. A known DNAPL volume in either a residual or pooled distribution was introduced in the theoretical porous medium. The purpose of the model was to simulate the injection, transport, retardation, and extraction of a partitioning tracer through the aquifer flow field. Once development of the model was complete, simulations were run to obtain the concentration breakthrough curves at the extraction wells for both partitioning and nonpartitioning tracers. This breakthrough data was then used to determine the average travel time (from the method of moments) of the various tracers between injection and extraction wells. The average travel times were input into Equation (12) to estimate the NAPL saturation in the porous medium. This value was then used in Equation (13) to estimate the volume of NAPL in the system. Comparisons of the model results to the known NAPL volumes as well as comparisons between the different distributions were made to assess the impact of NAPL distribution and average NAPL saturation on the accuracy of the tracer method.

GMS

GMS is a sophisticated graphical tool used for numerical modeling of groundwater systems. It was developed by Brigham Young University for the U.S. Army Waterway Experiment Station (WES). The software allows the user to construct two or three-dimensional representations of the subsurface environment. This can be accomplished by using one or a combination of the nine GMS modules to either create a scenario from scratch or incorporate information from real or theoretical borehole data. Once the geometry of a model is created, GMS requires the input of all necessary parameters to adequately describe the physical and chemical processes that will govern groundwater flow and contaminant transport. These parameters include all material properties of the aquifer solids (e.g., saturated hydraulic conductivity, pressure head profiles, moisture content profiles, dispersion coefficients, etc.), fluid properties, boundary conditions (e.g., no flow and constant head), sorption isotherms, sources and sinks (e.g., injection and extraction wells), and initial concentrations of contaminant.

To simulate contaminant (or in the case of this research, tracer) transport through the simulated aquifer, GMS supports complete interface with the MODFLOW and FEMWATER flow and transport codes. FEMWATER is a finite element transport model capable of simulating transport through both the vadose (unsaturated) and saturated zones. Although only the saturated zone is of interest in this research, FEMWATER was chosen because it allows the input of different retardation factors for different materials (i.e., for aquifer solids and NAPL contamination). FEMWATER also requires input to specify how solutions will be determined mathematically. This input includes such things as whether the solution will be transient or steady-state, the type of numerical method to be used and the iteration (time control) parameters. For the experiments in this research, a steady-state/flow only simulation was required in order to establish a flow field to conduct the tracer tests. Once this was complete, a transient/transport run was performed to simulate the tracer test.

Model Geometry

A finite element grid and a borehole file were required to create the model aquifer. The finite element grid was constructed directly from GMS and only required input of the dimensions of the desired system. The system used in this research was a 30 m x 30 m x 20 m rectangular porous medium. These dimensions were chosen because it was necessary to have a large enough volume for adequate retardation to occur but small enough to allow transport of the tracer within a reasonable length of time.

The borehole file is a text file that contains information from a series of theoretical borehole logs. Each borehole is described by a series of contacts which represent the boundaries between different subsurface materials. Because this was the first attempt in modeling the tracer experiments, the aquifer represented in this research was homogeneous (i.e., one material), consisting of a silty sand material. The borehole file used to create the geometries consisted of nine boreholes, ten meters apart in both the x and y directions and 20 meters deep (see Figure 1). Each hole consisted of two

Figure 1: Boreholes

layers consisting of the silty sand without NAPL and silty sand with NAPL ganglia or pools. A copy of the borehole text file is located in Appendix A. Once construction of the 3-D finite element mesh for the aquifer was complete, it was possible to modify the attributes of different elements in order to obtain the desired NAPL volume. The aquifer characteristics and dimensions modeled in this research were the same for all of the simulations. The only thing that changed for each scenario was the volume and configuration of the simulated NAPL contamination.

NAPL Distribution Scenarios

This study employed simple NAPL distributions to investigate the sensitivity of the breakthrough curve to NAPL volume and distribution. There were two distributions addressed in this research; simulated NAPL pools and simulated NAPL ganglia. The shape of the NAPL distributions resembled those created by Anderson et al. (1992). Their experiment involved modeling contaminant plumes from NAPL finger (ganglia) and pool sources. Ganglia sources were represented by a 3-D parallelepiped source configuration while pooled sources consisted of a thin rectangular shape. The geometries of these sources provided insight on how the NAPL could be represented within the 3-D mesh.

Once it was decided how the distributions would be simulated, it was then necessary to determine how much NAPL should be present. It was decided that two pool scenarios would be simulated consisting of different total NAPL volumes. Similarly, two residual scenarios were created containing the same total NAPL volumes as the pool simulations. The reason for this was to ensure that comparisons could be made between the two types of distributions and between the different volumes of NAPL (i.e., different average saturation values).

To determine the exact volume of NAPL for each scenario, the average NAPL saturation had to be estimated. A NAPL pool occupies a smaller volume of aquifer than an equivalent amount of NAPL distributed as ganglia. Therefore, a NAPL saturation for the distribution type had to be specified. Mercer and Cohen (1990) state that values of residual saturation generally range between 0.15 to 0.50; this research used a value of 0.30 for the ganglia distributions. For pools, the saturation is usually higher because the contamination is continuous. A saturation of 0.8 was chosen for the pool configurations. The “known” NAPL volume is thus determined by the following equation:

$$V_{NAPL} = \frac{S_{Navg}}{S_{Ndist}} \cdot V_{MEDIA} \tag{14}$$

where S_{Navg} is the average NAPL saturation of the aquifer, S_{Ndist} is the NAPL saturation for the particular distribution, and V_{MEDIA} is the total volume of the porous medium. Table 1 provides a summary of how the dimensions of the NAPL contamination for each scenario were determined. Figures 2 and 3 provide illustrations of cross sections of both types of distributions.

Tracer Selection

Both a nonpartitioning and partitioning tracer were required for these simulations. The type of tracer chosen has an impact on some of the material properties discussed later in this chapter (e.g., distribution coefficient (K_d) and molecular diffusion coefficient (D_w)).

The field experiment conducted by Annable et al. (1995) provided several examples of tracers that could be used in this study. Bromide (injected as KBr) was chosen as the non-partitioning tracer while n-Hexanol, with a K_{Nw} of 4.6, was chosen for the partitioning tracer. The value of K_{Nw} was determined from batch and column tests using the existing NAPL found at the test site. Therefore it is assumed that the NAPL in these simulations has the same partitioning coefficient as the NAPL in the Hill AFB field experiment.

Table 1: NAPL Distribution Dimensions

	S_{Ndist}	S_{Navg}	V_{NAPL} (m^3)	V_{MEDIA} (occupied by NAPL) (m^3)	Depth (m)	Area (m^2)
Ganglia	0.3	0.01	52.65	600	20	30
		0.001	5.265	60	20	3
Pools	0.8	0.01	52.65	225	0.36	625
		0.0009	4.717	20.16	0.36	56

Time and Output Control Parameters

The time control parameters dictate the total duration of the simulation as well as the iterative time step used to compute the solution. Based on the hydraulic conductivity, well injection and extraction rates, and the distance between the injection and extraction wells, the simulation time needed to be long enough to ensure the tracer would travel through the system. In field experiments, measuring methods would be limited to

Figure 2: Ganglia Distribution Cross Section

Figure 3: Pool Distribution Cross Section

detecting tracer concentration in extracted groundwater above a specific level (e.g., ≥ 1 ppb). Tracer tailing would result in concentrations below this level. Although the initial intent was to run the simulations until concentrations were below this threshold, the time required to do this was unreasonably long (i.e., over 10000 simulated hours). Therefore the total simulation times were basically determined from trial and error. For the nonpartitioning tracer tests, a simulation time of 4000 hours was sufficient while 8000 hours were needed for the partitioning tracer experiments. Also, a constant time step of ten hours was found to be small enough to ensure a stable solution.

Material Properties

GMS requires the input of several parameters to describe the subsurface properties that control the transport of the tracer through the porous medium. These properties must be specified for each material defined in the borehole file. Table 2 provides a summary of the input parameters required by GMS. Values in brackets are those that were not specified by GMS but were required in order to calculate other specified parameters. A brief explanation of each parameter is included below. Any calculations required are included in Appendix B.

Hydraulic Conductivity: A value of 0.45 m/hr was chosen for the saturated hydraulic conductivity of the silty sand. Because the aquifer in this study is homogeneous, the conductivity is the same in the x, y, and z directions. For soil containing NAPL ganglia, the hydraulic conductivity was determined from the θ_w value determined from Equation (15):

$$\theta_w = n - \theta_N \tag{15}$$

Using the moisture content profile of the silty sand, the pressure head value corresponding to θ_w was chosen. This value was then used to determine the corresponding conductivity value from the relative conductivity profile. Multiplying this value by the hydraulic conductivity of the silty sand yielded the value of conductivity for the soil with NAPL ganglia. The same approach was used for the soil with NAPL pool.

Table 2: Material Properties

	Silty Sand	**w/Ganglia**	**w/Pool**
n	0.2925	0.2925	0.2925
S_N	[0]	[0.3]	[0.8]
θ_N	[0]	[0.0878]	[0.234]
θ_w	0.2925	0.2048	0.0585
k	0.450 (m/hr)	0.2969 (m/hr)	0.0663 (m/hr)
ρ_B	1870 (kg/m^3)	1870 (kg/m^3)	1870 (kg/m^3)
α_L	0.60 (m)	0.750 (m)	0.750 (m)
α_H	0.060 (m)	0.075 (m)	0.075 (m)
D_w Br^- n-Hexanol	4.754 x 10^{-3} (m^2/hr) 4.753 x 10^{-3} (m^2/hr)	2.60 x 10^{-3} (m^2/hr) 2.60 x 10^{-3} (m^2/hr)	1.44 x 10^{-4} (m^2/hr) 1.15 x 10^{-4} (m^2/hr)
τ_w	0.660	0.289	0.016
K_d	0	2.16 x 10^{-4} (m^3/kg)	5.76 x 10^{-4} (m^3/kg)

Bulk Density: The bulk density of a soil is defined as the ratio of the weight of dry solids to the bulk volume of the soil. Maidment (1993) provided a chart of mineral bulk densities for several different soil types, from which a value was selected for this aquifer.

Dispersion: To allow the tracer to travel between injection and extraction at a reasonable rate, the objective was to have advective dominant flow. Therefore, a Peclet number of 50 was used to determine the longitudinal dispersion coefficient (α_L). The lateral (horizontal) dispersion coefficient (α_H) was assumed to be approximately one tenth of the longitudinal value. The silty sand with NAPL material had a higher dispersion coefficient for both ganglia and pools. This was because the low hydraulic conductivity of the areas containing NAPL reduces the groundwater velocity through those areas and thus adds mechanical dispersion (Dominico and Schwartz, 1990).

Molecular Diffusion Coefficient: The molecular diffusion coefficient (D_w) depends on what type of tracer is being used. These values were calculated by the method of Hayduk and Laudie (1974). The difference between the values for each tracer are due to the differences in molar volumes of the organic chemicals being considered.

Tortuosity: Maidment (1993) provides an equation that relates the tortuosity factor (τ_w) to the water content for each material in the system. This equation is:

$$\tau_w = \frac{\theta_w^{\frac{7}{3}}}{n^2} \tag{16}$$

Because θ_w for each material was different, τ_w varied for the silty sand, silty sand with ganglia, and silty sand with pool.

Sorption Coefficient: GMS requires the input of the K_d parameter when modeling sorption. In this research, NAPL partitioning was simulated as sorption. The K_d term had to be adjusted to account for the processes taking place. The sorption coefficient (K_d) was zero for the flow only/steady state simulations and the nonpartitioning tracer experiments. For the tracer experiments simulating n-Hexanol, Equation (17) was used to compute K_d for the silty sand with NAPL:

$$K_d = \frac{K_{Nw} \cdot \theta_N}{\rho_B} \tag{17}$$

Boundary Conditions

The field experiment by Annable et al. (1995), used four metal sheet piling walls to create a test cell that allowed the flow to be controlled by injection and extraction wells. Similarly, the simulations for this research used four “no flow” boundaries on the sides and a no flow boundary on the bottom. This helped alleviate concerns of stressing the boundary conditions with the wells necessary to perform the experiment. Figure 4 provides an example of a test cell containing a pool distribution.

In order to establish hydraulic control, a head boundary was required for FEMWATER to have a reference head value during the steady-state simulations. Once the head values are designated, water (and tracer) is allowed to flow through those areas. Therefore, in order to minimize loss of the tracer, only four nodes were specified as head boundaries. The four center nodes on the top layer were specified as constant elevation head values.

Injection and Extraction Wells

An injection and an extraction well was simulated using the point source/sink boundary condition command. This feature allowed the input of the well flow rates (positive for injection and negative for extraction) as well as the concentrations of tracer

Figure 4: Test Cell

injected versus time (i.e., tracer pulse). Active well points installed at every layer of the mesh to simulate the tracer being injected and extracted throughout the entire depth of the aquifer. Well flow rates were determined by trial and error steady state simulations. The rates were subsequently lowered until an adequate gradient with positive head values wasobtained. Head values needed to be positive to ensure that saturated conditions were simulated. The total pumping rate was 7.494 m^3/hr distributed evenly across the aquifer thickness (injection and extraction rates were the same). When a tracer was injected, the pulse length was 48 hours at a concentration of 10000 ppm for each well. Through the duration of the simulation, when tracer was not being injected, the wells were pumping in clean water.

<u>Conclusion</u>

Two tracer experiments were conducted for each scenario. The first consisted of the nonpartitioning tracer test and the second simulated a partitioning tracer with no sorption from aquifer solids. The results for these experiments are discussed in Chapter IV.

IV. Results and Analysis

Introduction

The object of interest from the FEMWATER simulations was the tracer breakthrough curve at each extraction well. The "gages" tool in GMS allowed the creation of the data sets (concentration vs. time) necessary to produce a breakthrough curve at each node designated as an extraction well. The data sets were then exported to a spreadsheet where further manipulation of the data was performed. The goal was to combine the data from the 16 extraction well points into one breakthrough curve representing the one extraction well. Figure 5 provides an example of breakthrough curves obtained for both a nonpartitioning and partitioning tracer. From this breakthrough data, moment analysis could be performed to obtain the values of t_p and t_n necessary for NAPL volume estimation.

Results

The zero moment calculation represents the amount of injected tracer mass recovered during the simulation. Dividing this value by the value of known mass injected gives the percent recovery for each experiment. Significant tailing (remaining mass) was evident for all of the simulations. Because it was unrealistic to run simulations long enough to ensure 100 percent mass recovery, an extrapolation of the remaining breakthrough curve was necessary to account for all of the tracer. A linear extrapolation to 100% mass recovery was performed for all of the simulations.

Figure 5: Breakthrough Curve

The extrapolated first moment ($m_{1,t}$') was calculated using Equation (18) as follows:

$$m_{1,t}' = \left[\frac{C_o \cdot t_{end}^{\,2}}{2} - \left(\frac{C_{last}}{t_{end} - t_{last}} \cdot \frac{t_{end}^{\,3}}{3} \right) \right] - \left[\frac{C_o \cdot t_{last}^{\,2}}{2} - \left(\frac{C_{last}}{t_{end} - t_{last}} \cdot \frac{t_{last}^{\,3}}{3} \right) \right] \qquad (18)$$

where C_o is the linearly extrapolated initial concentration, C_{last} is the concentration at the last time step in the simulation, t_{last} is the time at the last time step, and t_{end} is the extrapolated time at which all mass is removed. Equations (19) and (20) are used to determine the values of t_{end} and C_o, respectively:

$$t_{end} = \frac{m_{remain}}{0.5 \cdot C_{last} \cdot Q} \qquad (19)$$

$$C_o = C_{last} - \left(\frac{0 - C_{last}}{t_{end} - t_{last}} \cdot t_{last} \right) \qquad (20)$$

where m_{remain} is the mass remaining in the aquifer after the last time step, and Q is the total pumping rate (i.e. sum of all the well pumping rates).

Table 3 contains a summary of the values calculated from the moment analysis and the estimated volumes of NAPL for each set of simulations. The data used in the moment analysis for each scenario as well as the breakthrough curves for both Br- (nonpartitioning) and n-Hexanol (partitioning) are included in Appendix C.

Analysis

The effectiveness of the partitioning tracer test simulations were determined by comparing the values of V_{NAPL} obtained from the moment analysis to the known values input into the model (see Table 1). Table 4 provides a summary of how these values compared.

Table 3: Model Results (*denotes value determined from extrapolation)

scenario	zero moment (kg)	first moment (kg•hr)	recovery	travel time (hrs)	travel time* (hrs)	R	V_{NAPL} calculated (m^3)
ganglia (0.01)							
Br-	3053.02	2448891.18	0.85	802.12	2355.84*	1.23*	248.64*
n-Hexanol	3094.72	5901901.63	0.86	1883.09	2892.99*		
pool (0.01)							
Br-	3053.27	2374739.54	0.85	753.77	2195.50*	1.45*	467.68*
n - Hexanol	2942.13	10272194.7	0.82	3491.41	3180.06*		
ganglia (0.001)	3041.82	2254400.05	0.85	741.14	2235.23*	1.28*	300.89*
Br-	3093.97	6027238.34	0.86	1924.06	2858.48*		
n-Hexanol							
pool (0.0009)							
Br-	3050.27	2487218.33	0.85	791.41	1894.75*	1.72*	714.65*
n-Hexanol	2916.11	10570696.8	0.81	3624.93	3263.60*		

The results indicate that the NAPL volume for each scenario was largely overestimated. Perhaps the biggest reason for this was the fact that at least 15% of the tracer mass in each simulation was not recovered. Although some tailing should always be expected, there are two model specific factors that may have contributed to the difficulty in recovering the tracer. First, the constant head boundary condition required to

scenario	**V_{NAPL} (actual)** (m^3)	**V_{NAPL} (estimated)** (m^3)
ganglia (0.01)	52.65	248.64
pool (0.01)	52.65	467.68
ganglia (0.001)	5.265	300.89
pool (0.0009)	4.717	714.65

Table 4: Comparisons (Model Results vs. Input Values)

establish hydraulic control during the steady state simulations, created a “leak” at the top of the aquifer. Figure 6 illustrates an example of a velocity vector profile computed for a steady state solution with constant elevation head boundaries at the four designated nodes. The vector at the top points outward. Some tracer mass most likely escaped through this zone making it unrecoverable. However, it was not possible to determine exactly how much mass was lost. The inability to account for all of the tracer therefore adversely affected the ability to accurately conduct the mass balance for the simulations. The mass balance problems may have contributed to the high retardation factors computed from the moment analysis.

The other major factor that may have contributed to mass recovery problems was the existence of “dead zones” within the aquifer. These are locations where mass had difficulty moving due to the fact that they were relatively far from the influence of the well system. Dead zones were observed in the corners of the cell not containing

Figure 6: Velocity Vector Profile

any injection or extraction wells. Figure 7 depicts concentration contours for the final time step of the small pool (S_{Navg} = 0.001) simulation. The mass remaining in the corners supports the idea that zones do exist where mass seems to be "trapped". Poor mass recovery was at least partially due to the fact that tracer in these zones had not reached the extraction well.

Another factor that influenced the volume estimates was the uncertainty associated with the extrapolation technique used for calculating the first moment. This is related to the mass balance problems discussed above in that because the mass recovery was not complete for any of the simulations, extrapolation was necessary to ensure all of the mass was accounted for. Although linear extrapolation was used for simplicity, it is really impossible to know the exact behavior of the tracer for any given scenario. Therefore, any time an extrapolation is used, a certain degree of uncertainty in the results should be expected. Unfortunately, it is not possible to quantify the degree of uncertainty caused by the extrapolation. This prevents the ability to determine its exact impact on the simulation results.

Despite the mass recovery problems, the results do provide evidence of certain trends. The results suggest that the estimates for the ganglia scenarios were more accurate for both S_{Navg} values. One possible reason for this is that the ganglia distributions consisted of NAPL from the top to the bottom of the test cell. This included the region where the elevation head boundaries were specified (i.e., where the leak is expected to exist). Therefore, the low permeability of the NAPL may have resulted in

Figure 7: "Dead Zone" Concentration Contours

less mass escaping from the test cell. This would have provided a better mass balance and thus possibly a better estimation of the true NAPL volume.

It was expected that the partitioning tracer method would be more effective for the ganglia distributions (see Chapter 2). This was because the NAPL ganglia was expected to have better contact with the tracer. The reasons for this were that the geometry alone created more contact area for the tracer and the smaller NAPL saturation value had less of an impact on relative permeability of the contaminated soil. However, the fact that the retardation was larger for the pool distributions does not support the idea that NAPL ganglia had better contact with the tracer. Therefore, although the results do indicate that ganglia distributions provided more accurate tracer tests, the reason cannot be attributed to what was expected.

Results from the scenarios containing different S_{Navg} values are somewhat confusing. For both ganglia and pools, lower S_{Navg} values resulted in higher retardation factors (and thus higher NAPL volume estimates). It is intuitive that the opposite should occur. If less NAPL exists in the test cell, the retardation experienced by the tracer should also be less. Despite the end results, some of the interim results indicated what was expected. For example, the extrapolated average travel time of the nonpartitioning tracer was smaller for both distribution types. This was expected because the cells contained less volume of the low permeability silty sand with NAPL material. Therefore, it appears the problem stems from the simulations using n-Hexanol. This seems reasonable because the tailing effect (and thus the extrapolation uncertainty) is most likely greater for tracers experiencing retardation (i.e., partitioning tracers).

V. Conclusions and Recommendations

Introduction

The purpose of this research was to develop models to investigate the impact of NAPL distribution and saturation on the effectiveness of partitioning tracer tests for detecting and quantifying NAPL in the subsurface. GMS provided a means of creating 3-dimensional test cells capable of running partitioning tracer simulations using the FEMWATER transport code. The results of the simulations provided the necessary breakthrough data to estimate the volume of NAPL input into the models. Because the results from the simulations did not provide accurate estimates of the NAPL volume, it was difficult to assess the impact of distribution and average NAPL saturation (S_{Navg}) on the accuracy of the tracer method. However, this research did provide evidence of certain trends that relate to these factors. The work showed some of the problems associated with interpreting data generated from tracer tests and conducting mass balances necessary to account for all of the tracer mass (needed for accurate NAPL volume estimates). Finally, the work provided insight into possible modifications of the model that may help alleviate some of the problems encountered in this research.

Conclusions

The conclusions drawn from this research are summarized in the following statements:

1. The tailing effect of the tracer breakthrough curve created a significant problem when conducting moment analyses. Because it was not possible to predict what the remaining

breakthrough data would be, the uncertainty associated with the extrapolation technique was unavoidable. This appears to be the most likely cause of the high NAPL volume estimates. This problem is a significant concern for site investigators because available measurement limitations would create similar uncertainties in the breakthrough curves for actual field data.

2. Certain model parameters also contributed to mass balance problems. Constant head boundary conditions may allow tracer to flow out of the cell making it unrecoverable. Also, the particular well scheme used in the simulations may create "dead zones" that "trap" tracer mass. These limitations may have increased the uncertainty already associated with the first moment extrapolation method.

3. It was expected that the ganglia distributions would provide better results from partitioning tracer tests than pool distributions. Although this was the case, the hypothesis that increased contact area causes the phenomenon could not be verified by the research results. Corrections to the model may allow a more specific analysis on the impact of distribution type on the tracer method.

4. The results indicate that smaller NAPL volumes are more difficult to model for both distribution types. Despite having smaller NAPL volumes, the resulting breakthrough data indicated larger retardation factors than the simulations with higher S_{Navg} values. The mass balance problems that were evident in all of the simulations appear to have been more severe when less NAPL existed in the test cell. Alleviation of the mass balance limitations would most likely improve the ability to verify why the retardation was higher for these scenarios.

Recommendations

The following recommendations are included to provide insight into how to better model partitioning tracer experiments in order to alleviate the problems encountered during this research:

1. To estimate the amount of mass lost, the tracer concentration remaining at the last time step can be estimated by multiplying the concentration at each node by a finite volume around the node. Developing a mesh with uniform depth between nodes would help simplify this. Subtracting the mass injected by the amount recovered plus the amount remaining at the last step will yield an estimate of the mass lost.

2. Careful consideration should be given to assigning boundary conditions that do not contribute to tracer losses. One possible way would be to designate head boundaries to nodes that are perpendicular to the direction of flow (see Figure 8).

3. A well system should be developed that does not create the type of "dead zones" that existed in these models. This would involve multiple wells that have a combined radius of influence large enough to cover the entire flow field. An example of this is also included in Figure 8.

4. Sensitivity analysis should be performed on the various parameters (e.g. material properties) that GMS requires. This is especially important for parameters that differ significantly between different scenarios (e.g., S_{Ndist} and K_d). This may help discover what variables have the most impact on the results.

5. Sorption by aquifer solids is another important factor that requires further study. If the existing mass balance problems can be alleviated, GMS can be a useful tool for investigating the effects of sorption on the tracer method.

Figure 8: Recommended Head Boundary and Well Schematic

Appendix A: Borehole Log

Appendix B: Material Property Sample Calculations

Appendix C: Model Results